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WEAR REDUCING ADDITIVES

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U.S. ARMY ARMAMENT RESEARCH, DEVELOPMENT AND
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14. ABSTRACT An investigation into developing better additives for reducing gun barrel erosion was initiated by this laboratory. The investigation was prompted by the higher energy/density propellant formulations currently under development because these new propellants possibly could exacerbate gun barrel erosion. This report is a progress report that describes the initial results obtained with the U.S. Army Armament Research, Development and Engineering Center's, Picatinny Arsenal, New Jersey erosion test fixture. Some erosion mechanisms and proposed ways to reduce or interfere with them are discussed. Three candidates were selected: K ₂ CO ₃ , CaCO ₃ , and ZnCO ₃ and compared with the customary wear additive, TiO ₂ . Based on the data, it was concluded that all selected candidates reduced wear caused by both M30 and JA2 propellants, but K ₂ CO ₃ was ranked as most effective. The additives were also dispersed in silicone oil to form pastes. Five samples of K ₂ CO ₃ paste was loaded into an experimental obturator design and test fired in a 155-mm gun. The resulting 4% decrease in heat flux suggested that paste loaded obturators may be a feasible method to reduce gun barrel wear, but further investigation is necessary to verify this assertion.					
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INTRODUCTION

Over the years, the Army has been engaged in research and development programs dedicated either to improve the performance of existing weapon systems or to develop new higher performance weapon systems. This was usually addressed by employing hotter more energetic propellants.

However, the health and fitness aphorism, no pain no gain, accurately describes the evolutionary progress of enhanced gun performance. The gain in gun performance has been accompanied inevitably by increased gun barrel erosion. In this report, the terms wear and erosion will be used interchangeably.

In current high performance guns, the operating peak pressures are high [379.21 (55,000 psi) to 655.00 MPa (95,000 psi)]. In this high-pressure regime, the heating rates are also high, and as a result there is insufficient time for heat to be conducted away from the bore surface. In this case, the bore surface temperature can exceed the melting point of gun steel (1400-1500°C). The action of high-pressure hot combustion gases flowing across the surface wipes away any molten steel. The combined effects are usually referred to as the melt/wipe process.

On the other hand, in the low-pressure regime, heating rates are lower and there is ample time for heat to be conducted away from the bore surface. Hence, the bore surface temperature remains below the melting point of gun steel and the melt/wipe process does not occur. If any mass losses do occur in the low-pressure regime, they are much smaller than is observed in the high-pressure regime. Chemical reactions at the bore surface rather than the strictly thermal melt/wipe mechanisms are responsible for any small mass losses that are observed in the low-pressure regime (ref. 1).

Since the melt/wipe process is the major cause of gun barrel erosion in high performance guns, then one apparent approach to reduce or avoid the melt/wipe process would be to use high-energy propellants with lower flame temperatures. In a previous investigation (ref. 2), it was found that composite RDX propellants are more erosive than conventional propellants. In subsequent investigations (refs. 3 and 4), it was found that substitution of composite RDX propellants with lower flame temperatures for energy equivalent triple base or double base propellants resulted in greater erosion in the U.S. Army Armament Research, Development and Engineering Center's (ARDEC), Picatinny Arsenal, New Jersey erosion test fixture. This suggested that something in addition to propellant flame temperature alone should be addressed in the melt/wipe process.

Bore surface temperature is a function of both propellant flame temperature and the transport properties of the gaseous combustion products of the propellant. Composite RDX propellants produce combustion species that have a low average molecular weight. In general, low molecular weight species exhibit high thermal conductivities and low specific heats. Hence, low molecular weight species efficiently transfer thermal energy to the bore surface. Thus, the bore surface can attain higher temperatures with composite RDX propellants than it can with higher flame temperature double or triple-base propellants that produce higher molecular weight combustion products.

Another possible approach to achieve greater performance without increasing barrel wear would be to use larger propelling charges containing lower energy propellants. However, in view of current Army emphasis on greater weapon mobility, this is not a viable solution, because this would mandate larger combustion chambers and associated hardware that would significantly increase the weight of the weapon.

The wiping action in the melt/wipe process is a function of gas dynamics. That is, the manner in which the combustion gas flows over the bore surface affects the rate of barrel erosion. Turbulent gas flow over the molten surface during the ballistic cycle will produce greater barrel erosion than will smooth or laminar flow. A rough or irregular bore surface caused by pits and cracks will exacerbate turbulence. This increased turbulence results in accelerated localized gun barrel wear. This would be particularly important in chrome-plated gun tubes where surface cracks and heat checking are encountered.

Gun barrel wear in high performance guns can be reduced or, at the very least, constrained to acceptable limits by keeping the bore surface cool. An early attempt at cooling the bore in cased ammunition was the use of open-cell polyurethane foam liners (ref. 5). The barrel cooling mechanism was attributed to the laminar flow of cool gases generated by the combustion of the polyurethane liners.

The current popular approach to achieve barrel cooling has been to add selected metal oxides and silicates, normally referred to either as wear or erosion additives, to the propelling charge. The main function of these additives is to hinder heat transfer to the bore surface by depositing an insular metallic oxide layer on the bore surface.

Examples of traditional metal oxide wear additives are TiO_2 and TiO_2/wax (refs. 6 and 7). Both talc, which is a hydrated magnesium silicate, and a talc/wax mixture have also been used successfully as wear reducing additives (ref. 8).

These additives provide several different possible modes of reducing heat transfer to the bore surface. As already mentioned, the most obvious mode of action is thermally insulating the bore surface with a metal oxide layer during each shot. In addition, it may be possible for these insular layers to remain on the bore surface after each shot. This residual insular layer would also smooth the bore surface by filling pits and cracks that otherwise would act as local turbulence sites and exacerbate wear. One potential problem with this mode is that after many successive shots, the residual insular layer could build up to gun-fouling proportions.

Another possible mode of wear reduction for TiO_2 and talc additives was that they may introduce a cloud of motile solid particles into the combustion gas that shields the bore surface from radiant energy. Another possible mode was that the motile particles may also dampen the turbulent combustion gas flow. The collective effect of these modes was to lower the bore surface temperature while simultaneously reducing the wiping action of the combustion gases. This wear reduction mechanism was modeled by Buckingham, *et al* (ref. 9).

This laboratory initiated an investigation into finding more efficient wear additives. In addition, an investigation was started to find a more effective method to package additives in propelling charges. A necessary requirement for the package is to deliver the optimum quantity of additive at the proper time during the interior ballistic cycle. For some systems, the propelling charge has little or no room for wear-reducing additives. The feasibility of an alternate method of packaging optimum quantities of additives in these systems was also addressed.

EXPERIMENTAL

Erosion data were obtained with a 200-cm³ vented closed bomb modified to accept a gun barrel with a 0.95-cm (0.375-in.) bore and removable coaxial gun steel insert. This vented closed bomb will be referred to as the ARDEC erosion test fixture. Similar tests were attempted with chrome-plated gun steel inserts.

To measure the mass loss per shot due to erosion, the insert was cleaned and weighed before and after each shot. The mass loss was a measure of the bore surface wear.

The propellants used in this investigation were the M30 [1083 J/g Impetus and 3018K (2745°C) flame temperature] and the more energetic and erosive JA2 [1139 J/g Impetus and 3430K (3157°C) flame temperature]. All thermo-chemical data were obtained with the ARDEC thermochemical code MCVECE (ref. 10).

For each shot, the propelling charge was made by loading either M30 or JA2 propellant into the ARDEC erosion fixture. The desired peak pressure range for conducting this investigation was 137.90 to 172.37 MPa. This peak pressure was constrained to this pressure range by using constant charge weight (nominally 50 g) with selected web adjustment, and using a stainless steel 0.0056-cm burst disk placed between the barrel and the steel insert. For each additive shot, 4 g of additive were wrapped in a cellulose tissue and positioned in front of the propelling charge.

Pressure/time traces were obtained with a Nicolet digital oscilloscope connected to a pressure gage positioned inside the chamber.

Samples of K₂CO₃, modified K₂CO₃, CaCO₃, and ZnCO₃ were sent to Polysi Technologies, Inc., 1057 Jaycox Rd., Avon, Ohio 44011 to be dispersed in silicone oil. The resulting dispersions have grease-like and paste-like consistencies.

APPROACH

Only the melt/wipe mechanism was addressed in this effort and the mechanisms for the less significant gun barrel erosion were ignored. Hence, additive candidates were selected on the basis of potentially superior interference with the melt/wipe process.

Our guideline for selecting a more efficient candidate additive was that it should provide at least one wear-reducing mode in addition to the wear-reducing modes provided by TiO₂. Each candidate selection was based primarily on the assumption that it would generate a gas that would cool the bore surface while depositing a metal oxide insular layer onto the bore surface. Implicit in this cool gas assumption was that the generated gas must not react with the bore surface at the temperatures developed during the ballistic cycle. Based on this strategy, potassium carbonate (K₂CO₃), calcium carbonate (CaCO₃), and zinc carbonate (ZnCO₃) were selected as the initial gas generating wear additive candidates.





Inspection of reactions 1 through 3 reveals that these additives generate CO_2 and deposit solid metal oxides. The reaction temperature for ZnCO_3 (300°C) was almost 600°C lower than the reaction temperature for either K_2CO_3 (891°C) or CaCO_3 (898°C). It must also be emphasized that these are the calcination temperatures at atmospheric pressure rather than at the high pressures attained in the interior ballistic cycle. During the interior ballistic cycle, the temperatures should be somewhat higher.

The thermal properties of the deposited metal oxide also may affect the bore surface temperature. These thermal properties include thermal conductivity, heat capacity, thermal stability, and possible phase changes.

CaCO_3 occurs in nature as two different polymorphs, the orthorhombic low temperature form (aragonite) and a stable high temperature hexagonal form (calcite). Aragonite transforms endothermically into calcite at 520°C . TiO_2 has three polymorphs: brookite, anatase, and rutile. However, endothermic effects due to phase changes are not germane, because the stable high temperature polymorphs calcite and rutile were used exclusively in this effort.



The metal oxide K_2O initially decomposes (reaction 4) into liquid potassium and oxygen at 350°C . Since the decomposition of K_2CO_3 occurs at 891°C (reaction 1), this suggests that as soon as K_2O forms it decomposes into gaseous and liquid products, because potassium melts at 64°C and boils at 774°C . It seems reasonable to assume, barring any reaction with other chemical species, that little residual K_2O will remain after each shot, if the bore surface temperature exceeds 350°C for any length of time. In this thermal environment, successive consecutive shots would not substantially increase a K_2O insular layer on the bore surface. Thus for K_2CO_3 , its transient metal oxide insular layer probably does not play a significant role in the wear reduction mechanism. Consequently, the wear reduction rate would be approximately the same for each shot. However, despite the lack of metal oxide deposition on the bore surface, K_2CO_3 was still included as a potential wear additive to be evaluated.

On the other hand, metal oxides such as CaO , ZnO , and TiO_2 are thermally stable below 2580°C , 1975°C , and 1849°C , respectively (reactions 5 through 7). These decomposition temperatures are well above both the decomposition temperatures of their respective carbonates and the melting range of gun steel (1400 to 1500°C). This suggests that these metal oxides may remain deposited on the bore surface for some finite length of time provided other forces in the interior ballistic cycle do not remove them. In contrast to K_2CO_3 , the other deposited metal oxide insular layers could play a significant role in the wear reduction efficacy of CaCO_3 , ZnCO_3 , and TiO_2 .

Therefore, to eliminate or at least minimize the effect of residual metal oxide insular layers on wear efficacy, only data obtained from inserts cleaned between each shot were used for all additives. It will be left to future investigations to determine if residual insular layers actually result from a series of consecutive shots, and if, indeed, they do contribute significantly to wear reduction efficacy of the additive.

RESULTS AND DISCUSSION

M30 Propellant

Each propelling charge was composed of 50 g of M30 propellant in order to produce an average peak pressure in the range of 172.37 MPa (25,000 psi). A comparison of the wear reduction of each metal oxide and carbonate additive candidate and TiO_2 has for gun steel is presented in table 1. These data indicate that a 50-g propelling charge of M30 propellant loosely placed in the ARDEC erosion fixture produces on average a 20 mg/shot mass loss of gun steel. The addition of 4 g of K_2CO_3 wrapped in cellulose tissue and placed in front of the propelling charge reduces the mass loss to 10 mg/shot (50% mass loss reduction). The next best candidate, CaCO_3 , decreases the mass loss to 11 mg/shot (45% reduction), followed by TiO_2 with a mass loss of 12 mg/shot (40% reduction), and finally ZnCO_3 reduces the mass loss to 13 mg/shot (35% reduction). If only mass losses within one standard deviation are considered, then the relative efficacy ranking of the additives remains essentially the same. However, the reduction in mass loss for K_2CO_3 does decrease to 9 mg/shot (55% reduction), CaCO_3 remains at 11 mg/shot (45% reduction), TiO_2 remains at 12 mg/shot (40% reduction), and ZnCO_3 decreases to 12 mg/shot (40% reduction).

The data indicate that all the wear reducing additive candidates reduce erosion by at least 40%. However, K_2CO_3 is significantly more effective than TiO_2 , CaCO_3 is only marginally more effective than TiO_2 , and ZnCO_3 is less effective than TiO_2 . The next logical step would be to fire the more effective candidates in a weapon system that uses an M30-like propellant.

K_2CO_3 , in addition to being the best wear additive tested, is also a very effective flash suppressant (ref 11). However, there is one property of K_2CO_3 that complicates shelf life and field-testing, and that is that K_2CO_3 is deliquescent. This means that in a relatively humid environment, K_2CO_3 will absorb moisture continuously from the air until it dissolves completely in its own absorbed liquid water. If K_2CO_3 is packaged as dispersion in silicone oil, the absorbed water will eventually break down the dispersion. The rate at which this occurs is a function of the relative humidity. Short-term measures, such as an additive hermetically sealed in a plastic bag can be taken to protect K_2CO_3 from the environment during laboratory ballistic testing, but for long-term shelf life and field use these measures may be inadequate. However, a promising new method, which employs an admixture of a small quantity of hydrophobic material, is currently being investigated to resolve this problem.

JA2 Propellant

Each propelling charge was composed of approximately 50 g of JA2 propellant, which in this case produced an average peak pressure of 141.34 MPa (20,5000 psi). The data listed in table 2 indicates that JA2, which is more than 400K hotter than M30, produces on average an 87 mg/

shot mass loss. The addition of 4 g of K_2CO_3 reduces the mass loss to 58 mg/shot (33% wear reduction). The addition of 4 g of $CaCO_3$ reduces the weight loss to 69 mg/shot or a 21% reduction in wear. The addition of 4 g of $ZnCO_3$ reduces the wear to 77 mg/shot or a 12% wear reduction. The addition of 4 g of TiO_2 reduces weight loss to 60 mg/shot or a 31% wear reduction.

The erosion reduction values for CaO , ZnO , TiO_2 , and TiO_2 /wax in JA2 propellant are compared in table 3. TiO_2 , CaO , and ZnO reduce the wear/shot by 31%, 24%, and 17%, respectively. These metal oxides wear reduction values correlate with the values of their respective carbonates. This correlation suggests that if the metal oxide insular layer survives during repetitive shots, it will enhance the wear reduction effect of a carbonate additive.

Metal oxides are frequently formulated with wax in order to form a rigid matrix that can be conveniently made into a liner for propelling charges. The TiO_2 /wax 35% wear reduction value as opposed to 31% for TiO_2 demonstrates that wax enhances wear reduction in addition to providing a convenient packaging matrix to incorporate other wear reducing additives.

Additive Packaging

Two methods of packaging additives were initially considered. One method was additives dispersed in silicone oil and the other was additives mixed in wax. In this investigation, only silicone oil dispersions were studied.

The additives, 75% K_2CO_3 , 50% modified K_2CO_3 (non-hygroscopic), and 44% $CaCO_3$ were dispersed in a silicone oil to form paste-like suspensions. These suspensions will be referred to as pastes. Laboratory screening of the pastes in the ARDEC erosion test fixture was carried out with the pastes positioned in front of the charge. This configuration yielded erratic results. It was evident that while this configuration was satisfactory for screening solid additives, it was not good for pastes.

Rather than waste the limited supply of pastes on trial and error attempts to find the optimal paste configuration in the ARDEC erosion test fixture, it was decided instead to directly assess the feasibility of using pastes in a gun. This was done by piggybacking erosion testing onto scheduled 155-mm gun ballistic tests. A series of five shots using 50% modified K_2CO_3 (non-hygroscopic paste) was evaluated.

The propelling charges used in the ballistic tests had little room to incorporate significant amounts of additive. As a result of this lack of space, an alternate method that incorporates the additive in the projectile rather than in the propelling charge had to be used. The initially chosen method was to use the obturator as a means to deliver the paste onto the bore surface.

Five shots of modified K_2CO_3 (non-hygroscopic) paste were attempted with an experimental obturator designed by Kok Chung of ARDEC. In this design, the paste was loaded into an annular groove located in the outside edge of the obturator. Now the paste was forced to be in contact with the bore surface as soon as the projectile is seated into the gun.

Heat flux data were obtained from three pairs of thermocouples radially positioned about 180 deg apart and located at the axial positions, 45.854 in., 48.854 in., and 51.854 in. from the

RFT. The average heat flux from five shots with paste additive, and five shots without additive are compared in table 4. These data reveal that the paste additive produced an average 4% reduction in heat flux.

Although these initial tests used additives packaged as pastes and positioned in the obturator, this does not preclude that other additive packaging and/or other additive delivery systems might be more efficient.

However, these data do demonstrate that for propelling charges that have insufficient room to incorporate wear additives, it is possible to package enough additives on the projectile to reduce gun barrel wear.

Chrome-plated Inserts

Measurements of JA2 propellant erosivity with chrome-plated steel inserts were also attempted. Except for electro-polishing the insert bore surface, each insert was electroplated according to the protocol prescribed by Benet Weapons Laboratory, Watervliet, New York for electro-plating LC chrome on gun barrels. Massive weight losses were evident with the chrome-plated steel inserts. For some of them, weight losses were observed from the first shot and for others massive weight losses occurred after a few shots. Visual examination indicated extensive and progressive chrome plate spalling after each shot where massive weight losses were recorded.

One possible way to circumvent the chrome plate spalling problem in the ARDEC erosion test fixture was to use solid chromium inserts rather than chrome-plated steel inserts. However, the chromium insert does not necessarily mimic a chrome-plated insert or gun barrel, because there is no chromium/steel boundary in the chromium insert.

Chromium and steel have different thermal properties such as thermal conductivities, thermal expansion coefficients, and melting points. The many heating and cooling cycles encountered during repeated ballistic events may cause stresses at the interface between chromium and the steel substrate. These stresses, eventually, can seriously or even catastrophically impact chromium/steel adhesion, and ultimately jeopardize chrome-plate integrity. Hence, the lack of boundary effects in the chromium insert may cause its wear/time profile to be quite different from the chrome-plated and steel insert time/wear profiles.

Despite the fact that there were massive weight losses due to spalling that masked mask erosion mass losses, it may be possible to cull information about the erosion of the chrome plate. One approach is to compare the erosion profile of the steel insert with the erosion profiles of chromium and the chrome-plated steel inserts. The differences in chromium and chrome-plate wear profiles can be used to evaluate chrome-plate erosion. If spalling does not occur initially, the values for chromium erosion and chrome plated steel erosion should be equivalent (within experimental error). In this region of the wear profile mass losses, are due to chrome-plate erosion. If after a given number of shots, the chrome-plate erosion value becomes noticeably higher than the chromium insert erosion value, then spalling has begun to occur even if it is not noticeable to the naked eye.

An alternate approach to resolve this problem would be to design and fabricate a new erosion test fixture that would not spall coatings.

Future weapon systems that use different or more energetic/hotter propellants have potential gun barrel erosion problems. Each new system presents uniquely different erosion problems that are functions of propelling charge, barrel composition, and gun design. Hence, different barrel coatings, additives, and/or packaging will be required to effectively reduce gun barrel erosion in each new system. The U.S. Army Armament Research, Development and Engineering Center (ARDEC) erosion test fixture has the capability and versatility to evaluate the gun steel erosion of new propellants and the efficacy of candidate wear reducing additives. In 1984, this laboratory evaluated the erosion resistance of several exotic refractory metal alloys (ref 12). These alloys included tantalum/tungsten, and tungsten/carbon. The investigation revealed that some of the inserts coated with refractory metal alloys lost greater quantities of matter than did gun steel inserts. This was corroborated by visual evidence of spalling. These inserts spalled because they had insufficient titanium deposited on the steel substrate. A quality interfacial layer of titanium is necessary for proper adhesion of the subject refractory metal alloy to steel.

CONCLUSIONS

Based on the laboratory data, all the candidate additives reduce erosion. When using M30 propellant, a qualitative erosion reduction efficacy ranking of these candidates is $K_2CO_3 > CaCO_3 > TiO_2 > ZnCO_3$. For the hotter JA2 propellant, the ranking is $K_2CO_3 > TiO_2 > CaCO_3 > ZnCO_3$.

The highest ranked candidate, K_2CO_3 , probably does not deposit an insular oxide on the bore surface as do the other less effective candidates. However, wear reduction efficacy of the other additives may improve with repetitive firings because of the buildup of the metal oxide insular layer. This suggests that the mixture of K_2CO_3 with any of the other carbonates or TiO_2 may be more effective than any one of the candidates alone.

The paste additives do show promise, but further investigation with higher viscosity pastes and improved obturator design is necessary.

RECOMMENDATIONS

1. Test mixtures of K_2CO_3/TiO_2 , $K_2CO_3/TiO_2/Wax$, $K_2CO_3/CaCO_3$, $K_2CO_3/CaCO_3/wax$, $K_2CO_3/ZnCO_3$, and $K_2CO_3/ZnCO_3/wax$ in the U.S. Army Armament Research, Development and Engineering Center (ARDEC) erosion test fixture.
2. Develop more viscous pastes with putty-like consistencies.
3. Fire the best putty-like candidates in a 155-mm gun.
4. Repeat erosion measurements with chromium inserts.
5. Design and fabricate an erosion test fixture capable of measuring erosion of plated surfaces without spalling.
6. Evaluate erosion of M30 and JA2 propellants with chromium insert.
7. Evaluate erosion of propelling charge of current flight control system.

8. The proposed flight control system (FCS) currently configured to use a 120 mm gun with a tantalum coated barrel, and a JA2 propelling charge. To hasten the successful development of the current FCS or any subsequent improved version, the erosion characteristics should be addressed by evaluation in this laboratory with the ARDEC erosion test fixture.

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Table 1
Erosion of 4340 steel at 172.37 MPa using M30 propellant with and without 4 g of additives wrapped in cellulose tissue

Additive	Wt, g	Number moles	Weight loss/shot, mg	% loss	Weight loss /shot, mg	% loss
None	---	--	20	--	20	--
K ₂ CO ₃	4	0.03	10	50	9	55
CaCO ₃	4	0.04	11	45	11	45
ZnO ₃	4	0.03	13	35	12	40
TiO ₂	4	0.05	12	40	12	40

*Weight loss within one standard deviation.

Table 2
Erosion of 4340 steel At 141.34 MPa using JA2 propellant with and without 4 g of additives wrapped in cellulose tissue

Additive	Weight, g	Number of moles	Weight loss/shot, mg	% reduction
None	----	----	87	----
K ₂ CO ₃	4	0.03	58	33
CaCO ₃	4	0.04	69	21
ZnCO ₃	4	0.03	77	12
TiO ₂	4	0.05	60	31

Table 3
Erosion of 4340 steel at 172.37 MPa using 50 g propelling charges of JA2 propellant with and without 4 g of additives wrapped in cellulose tissue

Additive	Weight, g	Weight loss/shot, mg	% loss
None	----	87	----
CaO	4	67	24
ZnO	4	72	17
TiO ₂	4	60	31
TiO ₂ /W	4	57	35

Table 4
Five shot average heat flux at near the or for propelling charges with/without modified K₂CO₃ paste additive

Average heat flux BTU/Ft² for FIVE shots

Distance	45.854 in.	45.854 in.*	48.854 in.	48.854 in.*	51.854 in.	51.854 in.*
No Paste	118(5)	105(4)	109(2)	116(2)	104(2)	110(1)
Paste	111(2)	97((3)	106(2)	111(3)	101(2)	107(3)

*About 180 deg apart in the radial direction.

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